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(57) Abstract

Silica-based sols containing silica-based anionic particles having a high specific surface area and silica-based anionic particles having a low specific surface area. The sols can be prepared by mixing a sol containing silica-based anionic particles having a high specific surface area with a sol containing silica-based anionic particles having a low specific surface area. The sols are used as flocculating agents, in combination with amphoteric or cationic polymers, particularly in the production of paper and pulp but also for water purification.

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Silica-based sols, preparation and use of the sols

The present invention relates to silica-based sols containing silica-based anionic particles having a high specific surface area and silica-based anionic particles having a low specific surface area. The invention also relates to a method for producing the sols and to the use thereof as flocculating agents, in combination with amphoteric or cationic polymers, particularly in the production of paper and pulp but also for water purification.

Silica-based sols, which term is used herein for silica-based hydrosols, are aqueous systems with very small silica-based particles which can be used in several fields of application depending, inter alia, on the particle size. During recent years, silica-based sols with anionic silica particles of small particle size have gained an increased use in the production of paper. The silica sols are here used as additives to the stock in combination with amphoteric or cationic polymers, primarily to improve retention and dewatering.

European Patent 41056 discloses, for example, the use of colloidal silica sols in combination with cationic starch in papermaking. European Patents 185068 and 218674 disclose combinations of silica sols with particles where at least the surface groups contain aluminium, and cationic natural polymers and cationic polyacrylamides, respectively. The colloidal silica in these sols has a specific surface area of 50-1000 m^2/g. Commercially, use is generally made of sols of this type with discrete particles having a specific surface area of about 400-600 m^2/g, with an average particle size generally below 20 nm and most often ranging from about 10 down to about 1 nm. Sols with colloidal particles of the above-mentioned order of size have resulted in good retention and dewatering and have high stability. Quite generally, it has been desired for silica sols which are to be used commercially that they are as monodisperse as possible, i.e. that they have as narrow a particle size distribution as possible.

European Patent 491879 discloses silica sols having a degree of aggregate or microgel formation corresponding to an S-value of 8-45% containing silica-based particles with a specific surface area of 750-1000 m^2/g which are surface-modified

with aluminium to a degree of 2-25%.

The present invention relates to new silica-based sols containing silica-based anionic particles having a high specific surface area and silica-based anionic particles having a low specific surface area. It has been found that the sols according to the invention, in combination with cationic polymers, surprisingly give improved retention and dewatering results at the production of paper and similar products. A higher effect can be achieved with these sols than what could be expected from the included amount of the respective types of particles. With the sols according to the invention, silica-based particles having a comparatively low specific surface area, from about 50 to 400 m^2/g, i.e. a comparatively large average particle size, corresponding to from about 54 to about 7 nm, can also be used with good results. Silica-based sols with these larger particle sizes have themselves not given sufficiently good results to be used commercially within the field of retention and drainage.

The present invention thus relates to silica-based sols as further defined in the claims. The invention also relates to a method for producing silica-based sols and to the use of the sols as further indicated in the appended claims.

Silica-based particles, i.e. particles based on SiO_2, having a high specific surface area which can be used in the present sols include colloidal silica, colloidal aluminium-modified silica, aluminium silicate and different types of polysilicic acid. The particles can have a specific surface area within the range of from 425 to 1700 m^2/g, corresponding to an average particle size within the range of from about 6.4 to about 1.0 nm. The given specific surface area can be measured by titration with NaOH according to the method described by Sears in Analytical Chemistry 28(1956):12, 1981-1983. The average particle size of discrete spherical particles can be calculated from the relation 2720 divided by the specific surface area indicated in m^2/g, giving the average particle diameter in nm, as described by Iler in The Chemistry of Silica, pp 346-347, John Wiley & Sons, 1979. The specific surface area of the silica-based particles is suitably higher than 450 m^2/g and preferably higher than 475 m^2/g. The upper

limit for the specific surface area of the particles is suitably 1400 m^2/g and preferably 1200 m^2/g. An especially suitable range for the specific surface area is 750-1000 m^2/g, in particular 800-950 m^2/g.

Suitable silica-based particles having a high specific surface area are such particles which in silica-based sols result in an S-value within the range of from 8 to 90%, and preferably within the range of from 8 to 60%. The indicated S-value can be measured and calculated in accordance with what is described by Iler and Dalton in J. Phys. Chem. 60(1956), 955-957. The S-value indicates the degree of aggregate or microgel formation, where a low S-value indicates a higher microgel content, and can also be seen as a measure of the SiO_2 content, in % by weight, in the disperse phase.

The silica-based particles having a high specific surface area may be such particles which are described in the above-mentioned European Patents 41056 and 185068, which are hereby incorporated herein by reference, provided that the specific surface area lies within the indicated limits. Suitable particles described in these patents have a specific surface area of 425-1000 m^2/g. Particularly suitable silica-based particles having a high specific surface area originate from silica-based sols having an S-value within the range of from 8 to 45% containing silica-based particles with a specific surface area within the range of from 750 to 1000 m^2/g which are surface-modified with aluminium to a degree of from 2 to 25%. This type of particles and sols are disclosed in European Patent 491879, which is incorporated herein by reference. Further sols containing suitable silica-based particles are disclosed in European Patent 502089 and PCT Application WO 94/05596, which are also incorporated herein by reference. Suitable silica-based particles are also included in sols based on polysilicic acid, which means that the silicic acid material is in the form of very small particles, of the order of 1-2 nm, with a very high specific surface area, above 1000 m^2/g and up to about 1700 m^2/g, and with a certain degree of aggregate or microgel formation, which are described in European Patents 348366, 359552 and PCT Application WO 89/06637.

Silica-based anionic particles having a low specific surface area which can be used in the present sols include colloidal silica, colloidal aluminium-modified silica and aluminium silicate. These particles are suitably substantially spherical and preferably discrete, i.e non-aggregated, in contrast to microgel and aggregates, which contain aggregated particles, e.g. in the form of straight or branched chain-like formations. These silica-based particles can have a specific surface area within the range of from 50 to 400 m^2/g, suitably from 70 to 375 m^2/g, and preferably from 80 to 250 m^2/g. Sols with suitable silica-based particles having a low specific surface area can have an S-value within the range of from 25 to 95%, suitably at least 50%, and preferably from 60 to 95%. Sols with suitable silica-based particles having a low specific surface area are commercially available under the tradename Bindzil™, produced by Eka Nobel.

The sols of silica-based particles according to the invention may include silica-based particles having the high specific surface area in an amount of at least 50% by weight, suitably at least 60%, and preferably at least 75%, based on the total amount of silica-based particles. The upper limit of the included amount of high specific surface area particles is 99%, suitably 98%, preferably 95% and more preferably 90% by weight, based on the total amount of silica-based particles. Thus, the silica-based sols according to the invention may include the low specific surface area particles in an amount of from 1%, suitably from 2%, preferably from 5% and more preferably from 10% by weight, up to 50%, suitably to 40% and preferably to 25% by weight, based on the total amount of silica-based particles.

Sols according to the invention suitably have a dry solids content, calculated as SiO_2, of from 0.1 to 30% by weight. The dry solids content suitably exceeds 1%, preferably exceeds 3% and more preferably exceeds 5% by weight. Suitably, the upper limit is 25% and preferably 20% by weight. A major advantage of the present sols is that they can be prepared with higher dry solids contents and that an improved flocculation and dewatering effect can be obtained as compared with sols containing only silica-based particles having a specific

surface area within the range of 425-1700 m^2/g. As a result of the higher dry solids content of the stable sols according to the invention, the costs for storage and transportation can be significantly reduced. In papermaking, the improved dewatering obtained with the sols according to the invention means that the speed of the papermaking machine can be increased and, moreover, less water have to be removed in the press and drying sections of the machine, resulting in an substantially improved papermaking process.

The silica-based sols according to the invention can be prepared by mixing, suitably under agitation, a sol containing silica-based anionic particles having a high specific surface area as defined above with a sol containing silica-based anionic particles having a low specific surface area as defined above. Thus, the sols according to the invention can contain a mixture of a sol containing silica-based anionic particles having a high specific surface area within the range of from 425, suitably from 450, preferably from 475 and most preferably from 750 m^2/g, to 1700, suitably to 1400, preferably to 1200 and most preferably to 1000 m^2/g, and a sol containing silica-based anionic particles having a low specific surface area within the range of from 50 m^2/g, suitably from 70 and preferably from 80 m^2/g, to 400 m^2/g, suitably to 375 and preferably to 250 m^2/g. In the mixture, the sol containing silica-based particles having the high specific surface area can be included in an amount of from 50%, suitably from 60% and preferably from 75%, up to 99%, suitably to 98%, preferably to 95% and more preferably to 90% by weight, and the sol containing silica-based particles having the low specific surface area can be included in an amount of from 1%, suitably from 2%, preferably from 5% and more preferably from 10%, up to 50%, suitably to 40% and preferably 25% by weight, calculated on the total amount of silica-based particles. Sols of the respective types of particles within the defined specific surface area ranges that can be used in order to produce the sols according to the invention are known in the art and can be prepared by the skilled person.

When producing the sols according to the invention by this method, the sol with particles having the high specific

surface area suitably has a dry solids content, calculated as SiO_2, of 0.5-20% by weight, preferably 5-17% by weight, and the sol with particles having the low specific surface area may have a dry solids content of up to 60% by weight, suitably 3-60% and preferably 15-50% by weight.

The silica-based sols according to the invention may also contain hydrated particles of clays which are expandable in water and which are of the smectite type. Clays of the smectite type are thin flake-like, layered silicate minerals and comprise both naturally occurring materials and synthetic ones. The materials may be chemically treated, for example alkali-treated. The clays should be dispersible in water and thereby expand so that particles having a high surface area are obtained. Examples of clays of smectite type which are expandable in water and which can be used in the present sols are montmorillonite, bentonite, hectorite, beidellite, nontronite and saponite. Bentonite is preferred, and a suitable bentonite is, for example, the one described in European Patent 235893, which after swelling preferably has a surface area of from 400 to 800 m^2/g. The weight ratio of silica-based particles to clay particles can be from 20:1 to 1:10, based on dry matter. Suitably, the weight ratio ranges from 10:1 to 1:5, and preferably from 6:1 to 1:3. Aqueous mixtures of silica-based particles and clay particles according to the invention are stable and may have a dry solids content of from 1%, suitably from 5% and preferably from 8% by weight, up to 40%, suitably to 30% and preferably to 25% by weight

Silica-based sols according to the invention containing hydrated particles of clays which are expandable in water may, for example, be prepared by first mixing the clay into water and then adding a silica-based sol before the clay has had time to expand in the water, whereupon the aqueous mixture is well dispersed. It is however preferred that these mixtures be prepared by mixing the clay into a sol of silica-based particles and dispersing it well therein, using high shear forces. The sols used in the above-mentioned methods may be a silica-based sol according to the invention or a sol intended for the preparation thereof, whereby the mixture of clay particles and silica-based particles after the dispersing process is mixed

with additional silica-based sol in order to prepare the mixture according to the invention. Aqueous mixtures of silica-based particles and clay particles of the smectite type and the preparation thereof are disclosed in PCT Application WO 94/05595, which is hereby incorporated herein by reference.

The present sols are suitable for use as flocculating agents, for example in the production of pulp and paper and within the field of water purification, both for purification of different types of waste water and for purification specifically of white water from pulp and paper industry. The sols are used as flocculating agents in combination with cationic or amphoteric polymers, which may be natural, i.e. based on carbohydrates, or be synthetic. As examples of suitable polymers can be mentioned cationic and amphoteric starch, cationic and amphoteric guar gum, cationic and amphoteric linear and branched acrylamide-based polymers, cationic polyethylene imines, polyamido amines and poly(diallyl dimethyl ammonium chloride). The sols can be used with one or more polymers. As examples can be mentioned silica-based sol in combination with cationic starch and cationic polyacrylamide and sol in combination with low molecular weight highly charged cationic or amphoteric polymer and high molecular weight cationic polymer, especially cationic starch or acrylamide-based polymer. The sols can also be used in combination with polymers of opposite charges, such as sol in combination with cationic polymers, especially cationic starch, and anionic acrylamide-based polymer. Even if an arbitrary order of addition can be used, it is preferred that the polymer or polymers be added to pulp, stock or water before the sol.

A preferred field of use of the sols, in combination with polymer, is for improvement of retention and dewatering in papermaking. The terms "paper" and "papermaking" as used herein of course include not only paper and the production thereof but also other cellulose fibre containing sheets or web-like products, such as pulp sheets, board and paperboard and the production thereof. The sols are hereby suitably added to the stock in an amount of from 0.05 to 5 kg/ton, calculated as dry on dry stock system, i.e. fibres and optional fillers, and preferably in an amount of from 0.1 to 3 kg per ton. The

dry solids content of the sols when added to the stock is suitably adjusted to 0.1-10% by weight. For synthetic cationic or amphoteric polymers, use is usually made of at least 0.01 kg of polymer, calculated as dry matter per ton of dry stock system, and amounts of from 0.01 to 3 are suitably used and preferably from 0.03 to 2 kg per ton. For carbohydrate-based cationic or amphoteric polymers such as starch and guar gum, use is usually made of amounts of at least 0.1 kg/ton, calculated as dry matter per ton of dry stock system. Suitably, for these polymers use is made of amounts of from 0.5 to 30 kg/ton, preferably from 1 to 15 kg/ton.

When using sols according to the invention in the production of paper from a stock or suspension of cellulose containing fibres, and optional fillers, the invention further encompasses forming and dewatering the suspension in the presence of cationic or amphoteric polymers, e.g. those mentioned above, and a silica-based sol according to the invention comprising the mixture, in weight ratios as defined above, of a sol containing silica-based anionic particles having the high specific surface area as defined above, and a sol containing silica-based anionic particles having the low specific surface area as likewise defined above. Thus, the invention also encompasses separately adding to the stock the sol containing silica-based particles having the high specific surface area and the sol containing silica-based particles having the low specific surface area, in arbitrary order and at the same or different points.

The sols may, in combination with the polymers, be used in the production of paper from different types of stocks of cellulose-containing fibres such as stocks of fibres from chemical pulp, such as sulphate and sulphite pulp, chemo-thermomechanical pulp (CTMP), thermomechanical pulp, refiner pulp or groundwood pulp from both hardwood and softwood, and can also be used for stocks based on recycled fibres. Of course, the stocks may contain mineral fillers of conventional types, such as kaolin, titanium dioxide, gypsum, talc and both natural and synthetic calcium carbonates. Good results have also been obtained for stocks which are normally considered difficult. Examples of such stocks are those containing mecha-

nical pulp such as groundwood pulp, stocks based on recycled fibre pulp and stocks which due to the white water system contain high amounts of anionic impurities, such as lignin and dissolved organic compounds and/or high contents of electrolytes. As is well-known for silica-based sols as such, an improvement of the retention and dewatering effect can also be obtained for the present sols by adding aluminium compounds to the stock. Any in paper production per se known aluminium compound can be used, such as alum, aluminates, aluminium chloride, aluminium nitrate and polyaluminium compounds, such as polyaluminium chloride, polyaluminium sulphate and polyaluminium compounds containing both chloride and sulphate ions. The stock may of course also contain known hydrophobing agents, such as colophonium dispersions, or synthetic stock sizes, e.g. ketene dimer and alkenyl succinic anhydride dispersions.

The invention is further illustrated in the following Examples which, however, are not intended to limit the same. Parts and percentages relate to parts by weight and per cent by weight, respectively, unless otherwise stated.

Example 1

In this Example, silica-based sols according to the invention were prepared.

The following sols with silica-based particles having a high specific surface area were used:

A) A polysilicic acid of the type described in European Patent 348366 having a specific surface area of about 1400 m^2/g and a dry solids content of 1% by weight.

B) An anionic silica sol of the type described in European Patent 491879 having a comparatively low S-value, about 25, a specific surface area of about 900 m^2/g and being aluminium-modified to a degree of 5% with a dry solids content of 8.4% by weight.

C) An anionic silica sol of the type described in European Patent 41056. The sol was alkali-stabilised to a molar ratio of $SiO_2:Na_2O$ of about 40, and the particles had a specific surface area of 500 m^2/g, commercially available under the tradename BMA-0, Eka Nobel.

The following silica-based sols with particles having a low specific surface area were used:

D) An anionic silica sol having a specific surface area of 360 m^2/g and a dry solids content of 30% by weight, sold by Eka Nobel under the tradename Bindzil™ 30/360.

E) An anionic silica sol having a specific surface area of 220 m^2/g and a dry solids content of 40% by weight, commercially available under the tradename Bindzil™ 40/220.

F) An anionic silica sol having a specific surface area of 220 m^2/g and being aluminium-modified to a degree of 5% with a dry solids content of 30% by weight, commercially available under the tradename Bindzil™ 305.

G) An anionic silica sol having a specific surface area of 130 m^2/g and a dry solids content of 50% by weight, commercially available under the tradename Bindzil™ 50/130.

H) An anionic silica sol having a specific surface area of 80 m^2/g and a dry solids content of 30% by weight, commercially available under the tradename Bindzil™ 30/80.

I) An anionic silica sol having a specific surface area of 80 m^2/g and a dry solids content of 50% by weight, commercially available under the tradename Bindzil™ 50/80.

To a beaker equipped with a magnetic stirrer and containing 1.0 kg of sol with silica-based particles having a high specific surface area was added sol with silica-based particles having a low specific surface area in varying amounts, based on dry matter, as defined below. The sol mixtures were agitated for 10 min. The following sols were prepared:

Sol AE: 80% of sol A, 20% of sol E, dry solids content 1.2%
Sol AF: 80% of sol A, 20% of sol F, dry solids content 1.2%
Sol AG: 80% of sol A, 20% of sol G, dry solids content 1.2%
Sol AH: 80% of sol A, 20% of sol H, dry solids content 1.2%
Sol BE: 80% of sol B, 20% of sol E, dry solids content 10.0%
Sol BF: 80% of sol B, 20% of sol F, dry solids content 9.9%
Sol BG: 80% of sol B, 20% of sol G, dry solids content 10.1%
Sol BH: 80% of sol B, 20% of sol H, dry solids content 9.9%
Sol BI: 80% of sol B, 20% of sol I, dry solids content 10.1%
Sol BI90: 90% of sol B, 10% of sol I, dry solids content 9.4%
Sol BI95: 95% of sol B, 5% of sol I, dry solids content 8.8%
Sol CD: 80% of sol C, 20% of sol D, dry solids content 16.7%
Sol CI: 80% of sol C, 20% of sol I, dry solids content 17.4%

The sols according to the invention were stored for 1

week before being evaluated, and showed good stability.

Example 2

In this Example, a silica-based sol according to the invention containing bentonite was prepared.

A bentonite-containing sol having a dry solids content of about 9.0% was prepared from sol B according to Example 1 and sodium bentonite. The bentonite-containing sol was prepared from 152.5 g of sol B, 6.4 g of bentonite and 54.0 g of water. The ratio of silica particles to bentonite particles in this sol was about 2:1. The bentonite was added to sol B, and dispersion was carried out by means of an Ultra-Turrax at 10,000 rpm for 10 min.

To 100 g of the sol prepared as above was added sol I according to Example 1 in an amount of 7.9 g under agitation. The following sol was prepared in the indicated weight ratios, based on dry matter;

Sol BIb: 46.7% of sol B, 30.0% of sol I, 23.3% of bentonite, dry solids content 12.0% by weight

The resulting sol was stored for 1 week before being evaluated, and showed good stability. No bottom phase was formed, and the viscosity of the sol was substantially constant.

Examples 3-5

In these Examples, the dewatering effect was evaluated by means of a Canadian Standard Freeness (CSF) Tester, which is the conventional method for characterising dewatering or drainage capability according to SCAN-C 21:65. All additions of chemicals were made at a mixing speed of 800 rpm in a baffled Britt Dynamic Drainage Jar with a blocked outlet for 45 sec and the stock system was then transferred to the Canadian Standard Freeness Tester apparatus.

The stock was based on a CTMP pulp. 0.3 g/l of Na_2SO_4-$10H_2O$ had been added to the stock having a pH of 7.5. The stock concentration was 5.0 g/l. The CSF-value when no chemicals had been added was 200 ml. In all the tests, alum was added to the stock in an amount of 1 kg/ton, based on dry fibres, before the addition of cationic starch and silica-based sol. The cationic starch employed was a conventional medium-high cationised starch, Raisamyl 142, having a degree of substitution of 0.042. The cationic starch was added to the

stock in an amount of 8 kg/ton, based on dry fibres. The stock was agitated for 30 sec, whereupon silica-based sol was thereafter added in an amount of 1.0, 2.0 and 4.0 kg/ton, respectively, calculated as dry on dry fibres. After another 15 sec, the stock was transferred to the freeness apparatus.

Example 3 (Comparative tests)

The dewatering effect was examined for reference sols A, B, E, F, G and H according to Example 1. Table 1 shows the dewatering effect (ml CSF) for the sols added in different amounts (kg/ton).

Table 1

Amount kg/ton	Sol A ml CSF	Sol B ml CSF	Sol E ml CSF	Sol F ml CSF	Sol G ml CSF	Sol H ml CSF
1.0	615	610	535	530	500	460
2.0	620	625	600	600	555	525
4.0	625	630	630	625	600	580

Example 4

In this Example, the dewatering effect was evaluated for sols AE, AF, AG and AH according to the invention prepared in Example 1. Table 2 shows the results.

Table 2

Amount kg/ton	Sol AE ml CSF	Sol AF ml CSF	Sol AG ml CSF	Sol AH ml CSF
1.0	630	625	625	625
2.0	635	640	640	640
4.0	640	645	635	630

As is clearly evident from Table 2, improved dewatering was obtained with the sols according to the invention compared with sols A, E, F, G and H, respectively (Table 1), from which they are prepared.

Example 5

In this Example, the dewatering effect was evaluated for sols BE, BF, BG, BH according to the invention prepared in Example 1. Table 3 shows the results.

Table 3

Amount kg/ton	Sol BE ml CSF	Sol BF ml CSF	Sol BG ml CSF	Sol BH ml CSF
2.0	640	640	635	635
4.0	645	645	650	635

As is evident, all the sols resulted in a substantially higher dewatering effect than sols B, E, F, G and H, respectively, according to Table 1.

Examples 6-8

In these Examples, the dewatering effect was likewise evaluated by means of a Canadian Standard Freeness (CSF) Tester. The chemicals were added to a baffled Britt Dynamic Drainage Jar with a blocked outlet at 1000 rpm, and the stock system was then transferred to the freeness apparatus.

The stock was a standard stock based on a pulp composed of 60% bleached birch sulphate + 40% bleached pine sulphate. 30% chalk was added to the pulp as a filler, whereupon the pulp was diluted to a concentration of 4 g/l. 0.3 g/l of $Na_2SO_4.10H_2O$ was thereafter added. The stock had a pH of 8.1. In the tests, alum was added first in an amount of 1 kg/ton, based on dry stock system (fibres + filler), unless otherwise indicated.

The cationic polymer was a cationic starch of the same type as in Examples 3-5, which was added in an amount of 8.0 kg/ton of dry stock system. The stock was agitated for 25 sec, whereupon silica-based sol was added in amounts of from 0.5 to 1.0 kg/ton of dry stock system. After another 15 sec, the stock was transferred to the freeness apparatus.

Example 6

In this Example, the dewatering effect was evaluated for reference sols B and I and inventive sols BI95, BI90 and BI prepared in Example 1. Alum was not used in this Example. Table 4 shows the dewatering effect (ml CSF) for the sols added in different amounts (kg/ton).

Table 4

Amount kg/ton	Sol B ml CSF	Sol I ml CSF	BI95 ml CSF	BI90 ml CSF	BI ml CSF
0.5	450	270	-	470	455
0.75	470	300	490	500	-
1.0	500	325	515	520	500

The results show that the sols according to the invention resulted in a higher dewatering effect than sol B and I, respectively, from which they are prepared.

Example 7

In this Example, the dewatering effect was evaluated for reference sols C, D and I and inventive sols CD and CI prepared in Example 1. Table 5 shows the results.

Table 5

Amount kg/ton	Sol C ml CSF	Sol D ml CSF	Sol I ml CSF	Sol CD ml CSF	Sol CI ml CSF
0.5	465	385	270	485	470
1.0	565	475	325	565	560

As is evident, improved dewatering was obtained with the sols according to the invention as compared with sols C, D and I, respectively.

Example 8

In this Example, the dewatering effect was evaluated for the silica-based sol containing bentonite prepared in Example 2. Table 6 shows the results.

Table 6

Amount kg/ton	Sol BIb ml CSF
0.5	370
1.0	470
2.0	510

Claims

1. A silica-based sol, characterised in that it contains silica-based anionic particles having a high specific surface area within the range of from 425 to 1700 m^2/g and silica-based anionic particles having a low specific surface area within the range of from 50 to 400 m^2/g, the silica-based anionic particles having the high specific surface area being included in an amount of at least 50% by weight, calculated on the total amount of silica-based particles.

2. A silica-based sol, characterised in that it comprises a mixture of a sol containing silica-based anionic particles having a high specific surface area within the range of from 425 to 1700 m^2/g, and a sol containing silica-based anionic particles having a low specific surface area within the range of from 50 to 400 m^2/g, the sol containing silica-based anionic particles having the high specific surface area being included in an amount of at least 50% by weight, calculated on the total amount of silica-based particles.

3. A silica-based sol according to claim 1 or 2, characterised in that the silica-based anionic particles having the high specific surface area have a specific surface area within the range of from 450 to 1400 m^2/g.

4. A silica-based sol according to claim 1 or 2, characterised in that the silica-based anionic particles having the low specific surface area have a specific surface area within the range of from 70 to 375 m^2/g.

5. A silica-based sol according to claim 1, 2 or 4, characterised in that the silica-based anionic particles having the low specific surface area are substantially spherical, discrete particles.

6. A silica-based sol according to any of the preceding claims, characterised in that the sol contains silica-based particles having the high specific surface area in an amount of from 60 to 95% by weight, calculated on the total amount of silica-based particles.

7. A silica-based sol according to any of the preceding claims, characterised in that the particles

having the high specific surface area originate from a silica-based sol having an S-value within the range of from 8 to 45% and containing silica particles which have a specific surface area within the range of from 750 to 1000 m^2/g and which are modified with aluminium to a degree of from 2 to 25%.

8. A silica-based sol according to any of the preceding claims, characterised in that the sol further contains hydrated particles of clays of smectite type which are expandable in water.

9. A method for producing a silica-based sol, characterised in that it comprises mixing a sol containing silica-based anionic particles having a high specific surface area within the range of from 425 to 1700 m^2/g, with a sol containing silica-based anionic particles having a low specific surface area within the range of from 50 to 400 m^2/g, wherein the resulting sol contains silica-based anionic particles having the high specific surface area in an amount of at least 50% by weight, calculated on the total amount of silica-based particles.

10. Use of a silica-based sol containing silica-based anionic particles having a high specific surface area within the range of from 425 to 1700 m^2/g and silica-based anionic particles having a low specific surface area within the range of from 50 to 400 m^2/g, the silica-based anionic particles having the high specific surface area being included in an amount of at least 50% by weight, calculated on the total amount of silica-based particles, as a flocculating agent in combination with cationic or amphoteric polymers in the production of pulp and paper and for water purification.

11. Use according to claim 10, whereby the silica-based sol is used as a flocculating agent for improving retention and dewatering in papermaking.

12. Use according to claim 10 or 11, whereby the silica-based sol is used in combination with cationic starch or cationic acrylamide-based polymer or a combination thereof.

13. A process for the production of paper by forming and dewatering a suspension of cellulose containing fibres, and optional fillers, on a wire, characterised in that the suspension is formed and dewatered in the presence of

cationic or amphoteric polymers and a silica-based sol comprising a mixture of a sol containing silica-based anionic particles having a high specific surface area within the range of from 425 to 1700 m^2/g, and a sol containing silica-based anionic particles having a low specific surface area within the range of from 50 to 400 m^2/g, the sol containing silica-based anionic particles having the high specific surface area being included in an amount of at least 50% by weight, calculated on the total amount of silica-based particles.

14. A process according to claim 13, characterised in that the cationic or amphoteric polymers are selected from cationic starch, cationic acrylamide-based polymer and a combination thereof.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 95/00200

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: B01J 13/00, B01J 41/02, C02F 1/52
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 3867304 (MORRIS MINDICK ET AL), 18 February 1975 (18.02.75), claims 1-2 --	1-14
A	US, A, 4054536 (DAVID P. SCHAEFER ET AL), 18 October 1977 (18.10.77) -- --------	1-14

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" erlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
12 June 1995	21 -06- 1995
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Inger Löfgren Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

Information on patent family members

03/05/95

International application No.
PCT/SE 95/00200

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 3867304	18/02/75	NONE	
US-A- 4054536	18/10/77	NONE	